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(54) Deodorizer composition.

(57) A deodorizer composition comprising:

(a) an activated charcoal, a silica gel, a clay mineral, or an aluminosilicate having the following composition, in terms of oxides, represented by the composition ratio of the three components:

SiO<sub>2</sub>: 5 to 80 mole%;

MO<sub>n/2</sub>: 5 to 65 mole%;

Al<sub>2</sub>O<sub>3</sub>: 1 to 60 mole%

wherein M represents at least one metal selected from the group consisting of zinc, copper, silver, cobalt, nickel, iron, titanium, barium, tin and zirconium, and n represents a valence of metal; and

(b) at least one component selected from the group consisting of oxidizing agents, plant extracts, and germicides.

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## DEODORIZER COMPOSITION

## BACKGROUND OF THE INVENTION

## 1. Field of the Invention

The present invention relates to a deodorizer composition, more specifically, to a deodorizer composition having a strong deodorizing power which can be widely utilized to eliminate objectionable odors in the home and mitigate objectionable industrial odors generated by factories and the like.

## 2. Description of the Related Art

The increasing urbanization of formerly sparsely-populated areas has brought more people into daily contact with the various smells and odors of their environment, and this has led to a strong interest in, and severe criticism of, particularly offensive odors. Various methods of treating offensive odors are known in the art, of which the following are typical:

(1) Sensitive Deodorizing ... masking with perfumes or flavors;

(2) Physical Deodorizing ... adsorption with, for example, activated carbon or absorption or clathrating with, for example, cyclodextrin;

(3) Chemical Deodorizing ... neutralization with an acid or alkali, oxidation or reduction with an oxidizing agent or reducing agent, or an addition of, for example, lauryl methacrylate; and

(4) Biological Deodorizing ... deodorizing by germicidal action with germicide, or effects obtained with microorganisms or enzymes.

The sensitive deodorizing method is often unsuccessful since only the flavor of the odor is changed and the offensive odor itself is still present although masked, and thus if the balance between the offensive odor and the flavor is lost, the offensive odor again prevails and the balance must be restored.

In the physical deodorizing method, although the offensive odor is absorbed or clathrated, problems arise in that the adsorption power or clathrating power is not strong enough for practical use.

In the chemical deodorizing method, certain chemicals should not be used from the viewpoint of safety, and although a chemical deodorization of one offensive odor can be achieved, this same process will have no effect on the other various offensive odors generated in daily life.

In the biological deodorizing method, disadvantages in the deodorizing rate and a continuous effect or durability arise and, therefore, universal effects cannot be obtained by a single deodorizing method.

Conventionally activated carbon is most widely used, and is known as a deodorizer capable of adsorbing various offensive odor components. Nevertheless, among such offensive odor components, the capability of activated carbon for the adsorption of lower amines is small, and in particular, the deodorizing power thereof against hydrogen sulfide and ammonia is low.

Various attempts have been made to solve the above-mentioned problems. For example, JP-A-55-51421 (i.e., Japanese Unexamined Patent Publication) proposes that halides be supported on activated carbon;

JP-A-53-137089 proposes that metals be supported on activated carbon; and the adhesion or deposition of acids or alkalis has been studied. Nevertheless, these proposals are not still satisfactory.

Furthermore, although the above-mentioned patent publications generally describe deodorizing performances against various objectionable or offensive odors, the deodorizing speed (or rate) and the deodorizing amounts are also important factors, taking into consideration the utility of the deodorizer compositions.

The present inventors have proposed, in JP-A-63-220874, the use of aluminosilicates having a specified  $\text{SiO}_2$ ,  $\text{MO}_{n/2}$  and  $\text{Al}_2\text{O}_3$  composition in terms of the oxides expressed by the three component composition as a deodorizer.

## SUMMARY OF THE INVENTION

Accordingly, the objects of the present invention are to eliminate the above-mentioned disadvantages of the prior art and to provide a deodorizer composition exhibiting excellent deodorizing effects for various objectionable odors, and having a high deodorizing speed and safety.

Another object of the present invention is to provide a deodorizer composition exhibiting an excellent deodorizing effect for various objectionable odors, and an excellent persistency of the effect.

Other objects and advantages of the present invention will be apparent from the following description.

In accordance with the present invention, there is provided a deodorizer composition comprising:

- 5 (a) an activated charcoal, a silica gel, a clay mineral, or an aluminosilicate having the following composition, in terms of oxides, represented by the three component composition ratios:  
SiO<sub>2</sub>: 5 to 80 mole%;  
Mo<sub>n/2</sub>: 5 to 65 mole%;  
Al<sub>2</sub>O<sub>3</sub>: 1 to 60 mole%
- 10 wherein M represents at least one metal selected from the group consisting of zinc, copper, silver, cobalt, nickel, iron, titanium, barium, tin and zirconium, and n represents a valence of metal; and
- (b) at least one component selected from the group consisting of oxidizing agents, plant extracts, and germicides.

## 15 DESCRIPTION OF THE PREFERRED EMBODIMENT

The activated charcoal, silica gel, clay mineral, and aluminosilicate usable as the component (a) in the present invention preferably has a BET specific area of 100 m<sup>2</sup>/g or more, more preferably 500 to 2000 m<sup>2</sup>/g, when determined with N<sub>2</sub> gas.

Activated charcoal may be obtained by a treatment of, for example, coal, petroleum residue, charcoal, fruit, and shells, by the gas activation method using, for example, steam, carbon dioxide, or the chemical activation method using, for example, zinc chloride.

As the aluminosilicate, zeolite and those having the composition ratio of the three components represented in terms of oxides shown below are preferable:

25 SiO<sub>2</sub>: 5 to 80 mole%, preferably 25 to 75 mole%;  
Mo<sub>n/2</sub>: 5 to 65 mole%, preferably 15 to 60 mole%;  
Al<sub>2</sub>O<sub>3</sub>: 1 to 60 mole%, preferably 1 to 45 mole%  
wherein M represents at least one metal selected from zinc, copper, silver, cobalt, nickel, iron, titanium, barium, tin and zirconium, and n represents a valence of metal.

Of the component (a), aluminosilicates, in particular are considered to have the characteristics of a solid acid and solid acid group, and it has been reported that the acidity varies depending on the content of alumina in silica-alumina type catalysts, and that the acidity differs depending on the ratio of the contents of alumina and silica (Kozo Okabe: Acidic and Basic Catalysts, p. 183 (1967)). Further, since the aluminosilicate has a structure in which acidic SiO<sub>2</sub> and basic metal oxides are bound together, it has basic and acidic polarities and may be considered to exhibit deodorizing effect for objectionable odor components based primarily on a chemical adsorption and a chemical reaction.

The aluminosilicate is obtained as a white or pale-colored powder, and is prepared by allowing a water soluble silicate, a water-soluble metal salt, and further, a water-soluble salt aluminum salt and/or a water-soluble aluminate, in amounts corresponding to the above-mentioned composition ratio, to react in the presence of water, and if necessary, heating the precipitates obtained in the presence of water.

The above-mentioned reaction proceeds steadily due to a metathetical reaction. Namely, when an alkali silicate such as sodium silicate is used as a silica component, a water-soluble metal salt such as a chloride, nitrate, and sulfate is used as a metal oxide component, and further, sodium aluminate and/or a water-soluble aluminum salt such as aluminum chloride or aluminum sulfate are used as the alumina component, these components are mixed together in the presence of water, followed by effecting the metathetical reaction.

To uniformly effect the above-mentioned metathetical reactions, it is preferable to simultaneously add, to an aqueous dispersion containing silica previously dispersed therein, an aqueous silicate solution, an aqueous metal salt solution and an aqueous solution containing the alumina component, while allowing a reaction.

The above-mentioned metathetical reaction can be carried out at room temperature but, of course, also can be carried out upon heating at a temperature of up to, for example, about 95° C.

The preferable pH range of the reaction during the simultaneous addition is 5 to 10, most preferably especially 6 to 9. If necessary, the pH of the reaction mixture can be controlled by the addition of an acid or alkali, to maintain the above-mentioned pH range.

The above-mentioned simultaneous addition of the reactants allows the formation of precipitated aluminosilicate having a composition substantially corresponding to that of the aqueous solution. The

precipitates thus formed are separated, or optionally, are heated in the presence of water, to obtain a white or pale-colored fine powder.

As the oxidizing agent (i) of the component (b), chlorine dioxide, sodium hypochlorite, calcium hypochlorite, sodium dichloroisocyanurate, sodium p-chlorotoluenesulfonchloroamide, hydrogen peroxide, sodium percarbonate, potassium persulfate, potassium monopersulfate, sodium persulfate, ammonium persulfate, potassium permanganate, diperoxydodecane diacid, and magnesium perfumarate, are included as representative examples. Among the above, percarbonates, persulfates such as sodium persulfate, potassium persulfate, ammonium persulfate, and potassium monopersulfate; organic peracids such as diperoxydodecane diacid, and magnesium perfumarate, and salts thereof, are preferred.

As the plant extract (ii) of the component (b), an extract of a plant selected from red algae, brown algae, gymnosperms and angiosperms may be employed, preferably one having a deodorizing effect. Examples of such plants are as follows:

1) Rhodophyta

i) Gigartinales

a) Gracilariaceae - *Gracilaria verrucosa* Papenfuss

b) Gigartinaceae - *Chondrus ocellatus* Halmes

ii) Ceramiales

a) Rhodomelaceae - *L. Pinnata*, *L. Intermedia*

2) Phaeophyta

i) Chordariales

a) Chordariaceae - *Nemacystus decipiens* Kuckuck

ii) Laminariales

a) Laminariaceae - *Eisenia bicyclis* Setchell

iii) Fucales

a) Sargassaceae - *Hizikia fusiforme* Okamura, *Sargassum fulvellum* C. Agardh, *Sargassum horneri* C. Agardh, *Sargassum serratifolium* C. Agardh, *Sargassum thunbergii* O. Kuntze, *Sargassum serratifolium* C. Agardh, *Sargassum ringgoldianum* Harvey, *Sargassum patens* C. Agardh, *Sargassum tortile* C. Agardh, *Sargassum hemiphyllum* C. Agardh,

iv) Laminariales

a) Laminariaceae - *Undaria pinnatifida* Suringar

3) Gymnospermae

i) Ginkgoales

a) Ginkgoaceae - *Ginkgo biloba* L.

ii) Pinales

a) Taxodiaceae - *Metasequia*

4) Angiospermae

i) Piperales

a) Piperaceae - *Piper nigrum* L, *Cubebis*

ii) Fagales

a) Betulaceae - *Betula platyphylla* Sakatchev var *japonica* Ha

b) Fagaceae - *Quercus*

iii) Polygonales

a) Polygonaceae - *Rheum undulatum* L., *Polygonum Hydropiper* L

iv) Ranales

a) Magnoliaceae - *Magnolia Kobus* DC, *Magnolia obovata* Thunb

b) Ranunculaceae - *Paeonia suffruticosa* Andr., *Coptis japonica* Makino, *Cimicifuga simplex* Wormsk. var. *ramosa* Maxim.

v) Ranales

a) Lardizabalaceae - *Akebia quinata* Decne

b) Berberidaceae - *Nandina domestica* Thunb, *Epimedium macranthum* Morr. et Decne. Var. *violaceum* Franch

c) Lauraceae - *Cinnamomum camphora* Sieb

vi) Rhoeadales

a) Papaveraceae - *Papaver somniferum* L.

b) Cruciferae - *Isatis indigotica* Fortune

vii) Sarraceniales

a) Droseraceae - *Drosera rotundifolia* L

viii) Rosales

- a) Hamamelidaceae - Witch hazel
- b) Rosaceae - *Prunus donarium* Steb, *Duchesnea chrysantha* Miquel, *Crataegus cuneata* Sneb. et Zucc
- c) Leguminosae - *Cercis chinensis* Bunge, *Hedysarum esculentum* Ledeb
- ix) Geraniales
- 5 a) Rutaceae - *Xanthoxylum piperitum* DC., *Phellodendron amurense* Rupr.
- b) Meliaceae - *Melia azedarach* L. var. *japonica* Makino
- x) Parietales
- a) Theaceae - *Thea sinensis* L., *Camellia japonica* L.
- xi) Myrtiflorae
- 10 a) Punicaceae - *Punica grantum* L.
- b) Myrtaceae - *Syzygium aromaticum*, *Eucalyptus globulus* Labill, Myrtaceae *pimenta officinalis*
- xii) Umbelliflorae
- a) Umbelliferae - *Apium graveolens* L. *Anise pimpinella anisum*, *Nothosmyrnium japonicum* Miq
- xiii) Ericales
- 15 a) Ericaceae - *Pieris japonica* D. Don.
- xiv) Contortae
- a) Oleaceae - *Forsythia suspensa* Vahl.
- xv) Tubiflorae
- a) Labiatae - *Salvia officinalis* L., *Thymus, vulgaris*, *Origanum spp.*, *Rosmarinus officinalis* L., Skull-cap,
- 20 *Elsholtzia ciliata* Hylander, *Leonurus sibiricus* L., *Mentha spicata* L. var. *crispa* Benth, *Mosla dianthre* Maxim,
- Perilla frutescens* Britton Var. *acuta* Kudo, *Ocimum basilicum* L., *Origanum vulgare*, *Satureia ssp.*
- b) Solanaceae - *Lycium chinense* Mill
- c) Scrophulariaceae - *Picrorrhiza Kurroa* Rogl.,
- xvi) Rubiales
- 25 a) Rubiaceae - *Uncaria gambir* Roxb.
- xvii) Campanulatae
- a) Compositae - *Chicory*, *Arnica*
- xviii) Scitamineae
- a) Zingiberaceae - *Curcuma zedoaria* Roscoe, *Hedy chium spicatum* Hamilton

30 To obtain solvent extracts from these plants, as the plant, either the whole grass or the respective sections of plants such as leaves, plant skin, flowers, fruit skin, fruit, root stalk, or root may be employed, and the section containing relatively more of the deodorizing effective ingredient of the plant can be selected.

When obtaining deodorizing effective ingredients from these plants, known methods can be employed.

35 For example, it is possible to employ the method in which plants dried and then cut and formed into powder, are extracted with at least one polar solvent such as water, ethyl ether, ethylene chloride, dioxane, acetone, ethanol, n-butanol, ethyl acetate, propylene glycol or at least one nonpolar solvent such as n-hexane, petroleum ether, ligroin, cyclohexane, carbon tetra chloride, chloroform, dichloromethane, 1,2-dichloroethane, toluene, benzene, or a mixed solvent of these polar solvents and nonpolar solvents. In this

40 case, as the extraction operation, a conventional method can be employed in which, for example, plants are subjected to maceration in a solvent.

The extract obtained by the extraction operation as described above is usually formulated in a deodorizer after evaporation of the solvent, but in some cases, particularly when the solvent is water, ethanol can be also formulated as such in a deodorizer without evaporation of the solvent.

45 Examples of the germicide (iii) of the component (c) include p-oxybenzoate, o-phenylpheol, 3-methyl-4-isopropylpheol, bistributyltin oxide, dibutyltin naphthenate, triphenyltin oxide, benzetonium chloride, benzalkonium chloride,  $\alpha$ -bromocinnamic aldehyde, alkyl-di(aminoethyl)glycine salt, 2-bromo-2-nitropropane-1,3-diol, chlorohexidine, 2-(4-thiazolyl)benzimidazole, stearyl dimethylbenzylammonium chloride, distearyl dimethylammonium chloride, stearyl trimethylammonium chloride, cetylpyridium chloride, domiphen chloride,

50 alkylisoquinolium bromide, 3,4,4'-trichlorocarbanilide, dehydroacetic acid, sorbic acid, p-chloro-m-xylanol, p-chloro-m-cresol, 2,4,6-tribromophenol, 2,4,6-trichlorophenol, pentachlorophenol, 2,4,4'-trichloro-2'-hydroxydiphenyl ether, 3-trifluoromethyl-4,4'-dichloro-N,N'-diphenylurea, dimethyldithiocarbamate, 1,2-benzisothiazolin-3-one, butyl-m-cresol,  $\alpha$ -chlorobenzaldoxime acetate, resorcin, isopropylmethylphenol, and resorcin monoacetate. Among the above, p-chloro-m-xylanol, butyl-n-cresol, o-phenylpheol,  $\alpha$ -bromocinnamic aldehyde are preferred.

55

The deodorizer composition of the present invention can be obtained with the above components (a) and (b) as the essential components.

These respective components may be formed into powdery or granular products and mixed, the

component (a) may be impregnated with the component (b), and a carrier may be impregnated or attached with the component (b) and mixed with the component (a), or further, the components (a) and (b) may be kneaded and granulated under the condition maintained in a solvent.

In the deodorizer composition of the present invention, it is preferable to contain the component (a) and the component (b) at a weight ratio of  $(a)/(b) = 1/99$  to  $99.99/0.01$ , more preferably  $50/50$  to  $99.9/0.1$ , especially  $50/50$  to  $99.5/0.5$ . Also, if necessary, optional components can be further formulated in the composition.

In the composition of the present invention, in addition to the components (a) and (b), optional components such as surfactants, alkali agents, acid substances, dyes, UV-ray absorbers, antioxidants, and polymeric substances can be also formulated, if necessary.

A gas having an objectionable odor generally consists of a large number of components. As representative objectionable odor components, nitrogen type gases such as ammonia and amine, and sulfur type gases such as hydrogen sulfide and mercaptans, are known and are generated in large amounts. Nevertheless, since these nitrogen type and sulfur type objectionable odor components differ in behavior, an effective deodorizing base material for both objectionable odor components was not known.

In the present invention, by using the component (a) and the component (b), it is now possible to deodorize various objectionable odors. The performances demanded of deodorizers include, in addition to effects against various objectionable odors, a rapid deodorizing speed and large deodorizing capacity, i.e., long-term persistency.

In the present invention, the component (a), provides a deodorizing effect against various objectionable odors, and further, by using the component (b) in combination therewith, the deodorizing speed and the deodorizing capacity are improved.

Of the porous substances of the component (a), aluminosilicates in particular are considered to have the characteristics of a solid acid and solid acid group, and it has been reported that the acidity varies depending on the content of alumina in silica-alumina type catalysts, and that the acidity differs depending on the ratio of the contents of alumina and silica [Kozo Okabe: Acid Base Catalyst, p. 183 (1967)]. Further, since the aluminosilicate has a structure in which acidic  $\text{SiO}_2$  and basic metal oxides are bound together, it has basic and acidic polarities and is considered to exhibit a deodorizing effect against objectionable odor components based primarily on a chemical adsorption and chemical reaction.

On the other hand, porous substances having a specific surface area of  $100 \text{ m}^2/\text{g}$  or more as represented by activated charcoal have an excellent physical adsorption.

The deodorizing mechanism in the deodorizer composition of the present invention has not been defined, but it is considered that the physical adsorption proceeds at a very rapid speed until reaching an equilibrium, and subsequently, a chemical reaction occurs. That is, by combining a porous substance of the component (a) and the component (b), a rapid adsorption of objectionable odor onto a porous substance with a large specific area, and a chemical reaction of the adsorbed objectionable odor with the component (b), are considered to act synergetically, thereby effectively supplying a stronger deodorization effect.

Also, the objectionable odor trapped by the adsorption and chemical reaction will not be released as an odor, and it is considered that a release of an odor, which is a drawback of a deodorization by physical adsorption, is inhibited to improve the durability of the deodorizing effect.

According to the deodorizer composition of the present invention, by using the component (a) and an oxidizing agent (i) as the component (b) in combination, a stronger deodorizing power can be exhibited than in the case where each is used alone, but the deodorizing effect can be exhibited more rapidly and the persistency of the effect is prolonged.

In the present invention, by using the component (a), a plant extract (ii), and/or a germicide (iii) as the component (b) in combination, it is now possible to deodorize various objectionable odors.

Also, by using a plant extract (ii) of the component (b) in combination, in addition to eliminating various objectionable odors, a deodorizer composition is realized which has a rapid deodorizing speed, large deodorizing capacity, and a high safety factor.

Further, by combining a germicide (iii) of the component (b) with the component (a), the deodorizing speed and the deodorizing capacity are improved to provide a deodorizer having a prolonged persistency.

Therefore, although various objectionable odor components are exuded from the human body, in the home, and by industry facilities, the deodorizer composition of the present invention rapidly eliminates these objectionable odors and provides a long-term deodorizing effect, and thus can be widely utilized.

## EXAMPLE

The present invention will now be further, illustrated by, but is by no means limited to, the following synthetic Examples of the alumino silicates, Examples of the deodorizer compositions, and results of the evaluation thereof.

5

#### Synthetic Example 1

A 109 g amount of #3 sodium silicate ( $\text{SiO}_2$ : 22.0%,  $\text{Na}_2\text{O}$ : 7.0%) and 94 g of sodium hydroxide (NaOH content: 2.35 mole) were dissolved in water to prepare 1 liter of a solution A ( $\text{SiO}_2$  content: 0.4 mole).  
 10 Further, 95 g of zinc chloride (anhydrous salt) and 97 g of aluminum chloride (hexahydrate) were dissolved in water to prepare 1 liter of a solution B ( $\text{ZnO}$  content: 0.7 mole,  $\text{Al}_2\text{O}_3$ : 0.2 mole).

Then, one liter of water was charged into a 5 liter beaker and, while stirring, the solutions A and B were simultaneously added thereto at a feed rate of about 25 cc/min, respectively. The pH of the resultant reaction mixture was 6.9 after the addition.

15 The stirring was further continued, and after aging for 30 minutes, the mixture was heated at a temperature of 85 to 90 °C for 2 hours on a water bath. The reaction mixture thus obtained was filtered with aspiration, followed by washing with water and drying at a temperature of 110 °C, and the cake thus obtained was sifted through a sieve to obtain zinc aluminosilicate in the form of white particles having a size of 8 to 16 mesh (Tyler).

20 The composition of the three components and the BET specific surface of the resultant particles are shown in Table 2, together with the data of the following Synthetic Examples.

#### Synthetic Example 2

25

In the same manner as in Synthetic Example 1, 139 g of #3 sodium silicate ( $\text{SiO}_2$ : 22.0%,  $\text{Na}_2\text{O}$ : 7.0%) and 88 g of sodium hydroxide (NaOH content: 2.2 mole) were dissolved in water to prepare 1 liter of a solution A ( $\text{SiO}_2$  content: 0.51 mole). Further, 65 g of zinc chloride (anhydrous salt) and 126 g of aluminum chloride (hexahydrate) were dissolved in water to prepare 1 liter of a solution B ( $\text{ZnO}$  content: 0.48 mole,  
 30  $\text{Al}_2\text{O}_3$ : 0.26 mole).

Then, one liter of water was charged into a 5 liter beaker and, while stirring, the solutions A and B were simultaneously added thereto at a feed rate of about 25 cc/min, respectively. The pH of the resultant reaction mixture was 8.6 after the addition.

The reaction mixture obtained above was treated in the same manner as in Synthetic Example 1,  
 35 whereby zinc aluminum silicate in the form of particles having a size of 8 to 16 mesh was obtained.

#### Synthetic Example 3

40 A 273 g amount of #3 sodium silicate ( $\text{SiO}_2$ : 22.0%,  $\text{Na}_2\text{O}$ : 7.0%) and 60 g of sodium hydroxide (NaOH content: 1.5 mole) were dissolved in water to prepare 1 liter of a solution A ( $\text{SiO}_2$  content: 1.0 mole). Further, 34 g of silver nitrate and 225 g of aluminum nitrate (nonahydrate) were dissolved in water to prepare 1 liter of a solution B ( $\text{Ag}_2\text{O}$  content: 0.1 mole, Al content: 0.3 mole).

Then, one liter of water was charged into a 5 liter beaker and, while stirring, the solutions A and B were  
 45 simultaneously added thereto at a feed rate of about 25 cc/min, respectively. The pH of the resultant reaction mixture was 8.9 after the addition.

The stirring was further continued, and after aging for 1 hour, the cake thus obtained was sifted through a sieve to obtain silver aluminosilicate in the form of particles having a size of 8 to 16 mesh.

50

#### Synthetic Example 4

A 77 g amount of #1 sodium silicate ( $\text{SiO}_2$ : 35.0%,  $\text{Na}_2\text{O}$ : 17.5%) and 24 g of sodium hydroxide (NaOH content: 0.6 mole) were dissolved in water to prepare 1 liter of a solution A ( $\text{SiO}_2$  content: 0.45 mole).  
 55 Further, 216 g of zinc sulfate (heptahydrate) and 75 g of sodium aluminate ( $\text{Al}_2\text{O}_3$  content: 20.5%,  $\text{Na}_2\text{O}$  content: 19.5%) were dissolved in water to prepare 1 liter of a solution B ( $\text{ZnO}$  content: 0.75 mole,  $\text{Al}_2\text{O}_3$ : 0.15 mole).

Then, one liter of water was charged into a 5 liter beaker and, while stirring, the liquids A and B were

simultaneously added thereto at a feed rate of about 25 cc/min, respectively. The pH of the resultant reaction mixture was 6.9 after the addition.

The stirring was further continued, and after aging for 30 minutes, the mixture was heated at a temperature of 85 to 90 °C for 2 hours on a water bath. The reaction mixture thus obtained was filtered with aspiration, followed by washing with water and drying at a temperature of 110 °C, and the cake thus obtained was sifted through a sieve to obtain zinc aluminosilicate in the form of white particles having a size of 8 to 16 mesh.

#### Synthetic Examples 5 to 12

In the same manner as in Synthetic Example 3 (silver salt), aluminosilicates containing cobalt, nickel, iron, copper, titanium, barium, tin, and zirconium were obtained from the solutions A and B listed in Table 1.

Table 1

Compound	Synthetic Example No.							
	5	6	7	8	9	10	11	12
Solution A								
#3 Sodium silicate (mole SiO <sub>2</sub> )	273 g (1.0)	273 g (1.0)	273 g (1.0)	273 g (1.0)	273 g (1.0)	273 g (1.0)	273 g (1.0)	273 g (1.0)
Sodium hydroxide (mole NaOH)	60 g (1.5)	60 g (1.5)	60 g (1.5)	60 g (1.5)	60 g (1.5)	60 g (1.5)	60 g (1.5)	60 g (1.5)
Solution B								
Aluminum chloride*6H <sub>2</sub> O (mole Al <sub>2</sub> O <sub>3</sub> )	145 g (0.3)	145 g (0.3)	145 g (0.3)	145 g (0.3)	145 g (0.3)	145 g (0.3)	145 g (0.3)	145 g (0.3)
Cobalt chloride (mole CoO)	65 g (0.5)	-	-	-	-	-	-	-
Nickel chloride*6H <sub>2</sub> O (mole NiO)	-	120 g (0.5)	-	-	-	-	-	-
Ferric nitrate*9H <sub>2</sub> O (mole FeO)	-	-	200 g (0.5)	-	-	-	-	-
Copper chloride (mole CuO)	-	-	-	67 g (0.5)	-	-	-	-
Titanium sulfate (mole TiO <sub>2</sub> )	-	-	-	-	120 g (0.5)	-	-	-
Barium chloride*2H <sub>2</sub> O (mole BaO)	-	-	-	-	-	122 g (0.5)	-	-
Tin sulfate*2H <sub>2</sub> O (mole SnO)	-	-	-	-	-	-	126 g (0.5)	-
Zirconium chloride (mole ZrO <sub>2</sub> )	-	-	-	-	-	-	-	116.5 g (0.5)



Table 2

No.	Composition Ratio of Three Components			BET Specific Surface Area (m <sup>2</sup> /g)
	SiO <sub>2</sub>	MO <sub>n</sub> <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	
	(mole%)	(mole%)	(mole%)	
Synthetic Example 1	31	54	15	210
" 2	41	38	21	205
" 3	67	13	20	216
" 4	33	56	11	218
" 5	55	28	17	185
" 6	55	28	17	162
" 7	55	28	17	158
" 8	55	28	17	163
" 9	55	28	17	171
" 10	55	28	17	160
" 11	55	28	17	154
" 12	55	28	17	172

Example 1

Each of the aluminosilicates obtained in Synthesis Examples 1 to 12, activated charcoal manufactured by Mitsubishi Kasei K.K. (Diasorb G\*6-10) (specific surface area 900 m<sup>2</sup>/g), and various oxidizing agents shown in Table 3 were mixed to prepare deodorizer compositions (Present Products 1 - 12).

These products were evaluated by the evaluation methods shown below, and the evaluation results thereof are shown in Table 3 together with those of Comparative Examples.

Deodorizing Effect Evaluation Method A

Meat, vegetable, and fish were placed in a 6-liter desiccator and left to stand for 2 weeks to, prepare an artificial green garbage having an unpleasant odor.

A 5 g amount of the deodorizer composition was wrapped in a nonwoven cloth and placed in a wide mouth bottle to provide a sample. Further, from the 6-liter desiccator, 10 ml of the head space gas of the artificial green garbage odor was introduced into the wide mouth bottle, and the odor strength over a lapse of time was evaluated organoleptically, according to the following standards.

Evaluation point	Evaluation standard
0	no odor
1	very slight odor
2	slight odor
3	pervasive odor
4	strong odor
5	very strong odor

The evaluation was conducted by an expert panel of 5 members. The evaluations made by the top and bottom members were ignored, and an average of the evaluations made by the remaining three members was obtained by rounding off.

Table 3

Deodorizer Composition			Evaluation results over lapse of time		
Component (a)	Component (b) (oxidizing agent)	Formulation amount (Z) (a)/(b)	After 1 hr	After 3 hrs	After 6 hrs
Example 1 (Present product)	Activated charcoal	97/3	3	1	0
2	Potassium monopersulfate	50/50	3	1	0
3	Synthetic 1 Example	8/92	2	1	0
4	Hydrogen peroxide	90/10	2	1	0
5	Potassium persulfate	95/5	1	0	0
6	Magnesium-perphthalate	3/97	1	0	0
7	Potassium permanganate	80/20	2	1	0
8	Diperoxy dodecane diacid	55/45	1	0	0
9	Potassium monopersulfate	60/40	1	0	0
10	Sodium p-toluenesulfon chloroamide	92/8	2	1	0

Table 3 (Continued)

Deodorizer Composition			Evaluation results over lapse of time			
	Component (a)	Component (b) (oxidizing agent)	Formulation amount (Z) (a)/(b)	After 1 hr	After 3 hrs	After 6 hrs
Example (Present product)	11	Synthetic Example 9	10/90	1	0	0
	12	" 10	Ammonium persulfate	30/70	1	0
	13	" 11	Chlorine dioxide	99/1	2	1
	14	" 12	Sodium dichloroisocyanurate	99.5/0.5	1	0
Comparative Example	1	Activated charcoal	100/0	4	3	2
	2	-	Calcium hypochlorite	4	3	3
	3	-	-	5	5	5

Example 2

A mixture of 90 g of the aluminosilicate obtained in Synthesis Example 1 and 10 g of potassium persulfate was kneaded with 50 g of water, by a mortar, followed by drying at 80 °C to obtain a cake. The cake was crushed and sifted through a sieve to obtain a deodorizer composition as a white powder of 4 to 8 mesh (Present Product 15).

The results of the evaluation of this composition are shown below in Table 4, together with the results of Example 3.

Example 3

A mixture of 95 g of silica powder, 5 g of sodium percarbonate was kneaded with 50 g of water, by a mortar, followed by drying at 80 °C to obtain a cake. The cake was crushed and sifted through a sieve to obtain a white powder of 4 to 8 mesh. The white powder and the aluminosilicate obtained in Synthesis Example 2 were mixed to a formulation ratio of 9:1 to obtain a deodorizer composition (Present Product 16).

The deodorizing effect was evaluated according to the evaluation method described in Example 1, and the results of the evaluations of Examples 2 and 3 are shown in Table 4.

Table 4

	Deodorizer composition		Evaluation results over lapse of time		
	Component (a)	Component (b) (oxidizing agent)	After 1 hr	After 3 hrs	After 6 hrs
Present product 15	Synthetic Example 1	Potassium persulfate	1	0	0
" 16	" 2	Sodium percarbonate	1	0	0
Comparative Example 4	Activated charcoal	-	4	3	2
" 5	-	-	5	5	5

Example 4

A 2 g amount of dried leaves of rosemary was crushed by a cutter, charged into a Soxhlet extractor, and subjected to hot extraction with an addition of 180 g of water for 15 hours, whereby a 10% rosemary extract was obtained.

A 100 g amount of the aluminosilicate obtained in Synthesis Example 1 was impregnated with the 10% Rosemary extract and dried at 80 °C, and the cake thus obtained was sifted through a sieve of 8 to 16 mesh to obtain a deodorizer composition.

Example 5

A 20 g amount of the whole grass of thyme was crushed, charged into a Soxhlet extractor, and subjected to hot water extraction with an addition of 180 g of water for 13 hours to obtain an extract. A deodorizer composition was obtained in the same manner as in Example 4.

Example 6

A 10 g amount of leaves of dried sage was crushed, charged into a Soxhlet extractor, and subjected to

hot extraction with an addition of 190 g of 50% ethanol for 15 hours to obtain a 5% sage extract. An amount of 100 g of the aluminosilicate obtained in Synthesis Example 2 was impregnated with 10 g of the 50% sage extract obtained by concentration by an evaporator, followed by drying at 110 °C. The cake obtained was sifted through a sieve of 8 to 16 mesh to obtain a deodorizer composition.

#### Example 7

The 10% rosemary extract obtained in Example 4 was sprayed onto 100 g of the aluminosilicate obtained in Synthesis Example 3 to obtain a powdery deodorizer composition.

#### Example 8

The 10% rosemary extract obtained in Example 4 was sprayed onto activated charcoal (manufactured by Mitsubishi Kasei K.K.; Diasorb G-6-10) to obtain a powdery deodorizer composition.

#### Example 9

The sage extract obtained in Example 6 was sprayed onto spherical silica to obtain a deodorizer composition.

#### Example 10

A 30 g amount of pine leaves was crushed, charged into a Soxhlet extractor, and subjected to hot extraction with an addition of 150 g of acetone for 10 hours to obtain an extract. A deodorizer composition was the obtained by the same treatment as used in Example 4.

#### Evaluation of the Deodorizing Effect (Examples 4 - 10)

The deodorizer compositions of Examples 4 to 10 were evaluated according to the above-mentioned evaluation method A.

The results are shown in Table 5.

Table 5

	Sample	Deodorizing effect		
		1 hr	3 hrs	6 hrs
Present product	Example 4	1	0	0
	" 5	2	1	0
	" 6	1	0	0
	" 7	1	0	0
	" 8	3	1	0
	" 9	3	1	0
	" 10	2	1	0
Comparative Example	6 (10% Rosemary extract)	4	4	3
	7 (Activated charcoal)	4	3	3
	8 (50% Sage extract)	4	4	3
	9 (Blank)	5	5	5

Examples 11 - 18

The aluminosilicates obtained in Synthesis Examples 1 to 3, activated charcoal manufactured by Mitsubishi Kasei K.K. (Diasorb G-6-10), and various sterilizers shown in Table 6 were mixed to prepare deodorizer compositions.

These were evaluated according to the following evaluation method (method B), and the evaluation results thereof are shown in Table 6 together with those of Comparative Examples.

Deodorizing Effect Evaluation Method B

Meat, vegetables, fish, were placed in a 6-liter desiccator and left to stand for one week, to prepare an artificial green garbage. An amount of 30 g of the green garbage prepared was placed into a wide mouth bottle of 1.8-liter, 10 g of the deodorizer composition sprayed thereon, and the odor intensity over a lapse of time was evaluated organoleptically according to the following standards.

Evaluation point	Evaluation standard
0	no odor
1	very slight odor
2	slight odor
3	pervasive odor
4	strong odor
5	very strong odor

Evaluation was conducted by an expert panel of 5 members. The top and bottom members were ignored, and an average of the evaluations of the remaining three members was obtained by rounding off.

Table 6 (Continued)

Comparative Example	Deodorizer Composition		Evaluation results over lapse of time					
	Component (a)	Component (b) (Germicide)	Formulation ratio (a)/(b)	After				
				1 hr	3 hrs	6 hrs	1 day	2 days
10	Activated charcoal	-	100/0	4	3	2	2	3
11	-	Benzalkonium chloride	0/100	4	3	3	3	3
12	Activated charcoal	Methyl p-oxybenzoate	99.995/0.005	4	3	2	2	2
13	Silica powder	-	100/0	4	3	3	3	4
14	-	-	-	5	5	5	5	5

Table 6

Deodorizer Composition			Evaluation results over lapse of time				
Component (a)	Component (b) (Germicide)	Formulation ratio (a)/(b)	After 1 hr	After 3 hrs	After 6 hrs	After 1 day	After 2 days
Example 11 (Present product)	Activated charcoal	Benzalkonium chloride	99/1	3	1	0	0
12	"	o-Phenylphenol	99.9/0.1	2	1	0	0
13	"	2-(4-Thiazolyl)benzimidazole	50/50	2	1	0	0
14	Synthetic Example	3-(4-Chlorophenyl)-1-(3,4-dichlorophenyl)urea	90/10	1	0	0	0
15	"	2,4,4'-Trichloro-2'-hydroxy diphenyl ether	97/3	2	1	0	0
16	"	p-Chloro-m-xyleneol	95/5	1	0	0	0
17	"	Dehydroacetic acid	70/30	3	1	0	0
18	"	$\alpha$ -Bromocinnamic aldehyde	97/3	2	1	0	0



Example 19

A 100 g amount of the aluminosilicate obtained in Synthesis Example 1 was impregnated with 50 g of a 0.2% ethyl alcohol solution of 2-(4-thiazolyl)benzimidazole, and dried at 80 °C for one hour to obtain a powdery deodorizer composition.

Example 20

Onto 50 g of activated charcoal (manufactured by Mitsubishi Kasei, Diasorb G-6-10) was sprayed 10 g of an aqueous 30% benzalkonium chloride, to obtain a powdery deodorizer composition.

The deodorizing effect of the deodorizer compositions of Examples 19 and 20, was evaluated according to the method B. The results are shown in Table 7.

Table 7

	Deodorizer composition		Evaluation results over lapse of time				
	Component (a)	Component (b) (Germicide)	After 1 hr	After 3 hrs	After 6 hrs	After 1 day	After 2 days
Example 19	Synthetic Example 1	2-(4-Thiazolyl)benzimidazole	1	0	0	0	0
" 20	Activated charcoal	Benzalkonium chloride	3	1	0	0	0
Comparative Example 15	Activated charcoal	-	4	3	2	2	3
" 16	-	-	5	5	5	5	5

Example 21

5 A 100 g amount of the aluminosilicate obtained in Synthesis Example 3 was impregnated with 30 g of 10% ethyl alcohol solution of o-phenylphenol, and dried at 80 °C for 30 minutes to obtain a powdery deodorizer composition.

10 When the deodorizer composition was sprayed into a polymer bucket and a triangular sink-corner container for garbage, containing green garbage, the odor generated from the green garbage or remaining foods was eliminated.

Examples 22 - 28

15 Samples of each of the wastewaters shown below were placed, to an amount of one liter, in a 1.8-liter glass bottle.

Wastewater-A: washed wastewater from pig sty (feeding 87 pigs)

Wastewater-B: wastewater from cleaning tank of a standard family having 4 members.

20 Then 10 g of the deodorizer composition shown in Table 5 was added thereto, and the odor intensity over a lapse of time was organoleptically evaluated. The evaluation standards were made according to method B.

The deodorizer composition was a powdery product obtained by impregnating the aluminosilicate obtained in each Synthesis Example with an ethanolic solution of the sterilizer, followed by drying at 80 °C  
25 for one hour, and supplemented with 1% of sterilizer.

Table 8

	Deodorizer composition		Treated waste water	Evaluation results over lapse of time				
	Component (a)	Component (b) (Germicide)		After 1 hr	After 3 hrs	After 6 hrs	After 1 day	After 2 days
Example 22	Synthetic	p-chloro-m-xylenol	A	2	1	0	0	0
" 23	" 3	o-phenylphenol	B	2	1	0	0	0
" 24	" 1	2-(4-thiazolyl)benzimidazole	B	2	1	0	0	0
" 25	" 2	Dehydroacetic acid	B	3	1	0	0	0
" 26	" 2	o-phenylphenol	A	2	1	0	0	0
" 27	" 3	Benzalkonium chloride	A	3	1	0	0	0
" 28	" 2	Butyl m-cresol	A	2	1	0	0	0
Comparative Example 17	Silica	-	B	4	3	3	3	4
18	-	Dehydroacetic acid	B	4	3	3	3	3
19	Activated charcoal	-	A	4	3	3	3	4

Examples 29 - 31

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Onto 10 g of the aluminosilicate obtained in Synthesis Examples 1 - 3, 2 g of the 10% rosemary extract was sprayed and dried at 80° C for 3 hours, and the sample obtained was mixed with 0.3 g of a sterilizer to obtain a deodorizer composition.

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The evaluations were made according to the evaluation method (method B), and the evaluation results are shown in Table 9 together with Comparative Examples.

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Table 9

Deodorizer composition			Evaluation results over lapse of time					
Component (a)	plant extract (b)(ii)	Germicide (b) (iii)	After 1 hr	After 3 hrs	After 6 hrs	After 1 day	After 2 days	
Example 29	Synthetic Example 3	Rosemary	2	1	0	0	0	
" 30	" 1	"	2	1	0	0	0	
" 31	" 2	"	2	1	0	0	0	
Comparative Example 20	-	-	4	3	2	2	3	
" 21	Activated charcoal	-	4	3	3	3	3	
" 22	-	Rosemary	3	2	2	2	2	

# Claims

- 5 1. A deodorizer composition comprising:
  - (a) an activated charcoal, a silica gel, a clay mineral, or an aluminosilicate having the following composition, in terms of oxides, represented by the composition ratio of the three components:  
 $\text{SiO}_2$ : 5 to 80 mole%;  
 $\text{Mo}_{n/2}$ : 5 to 65 mole%;  
 $\text{Al}_2\text{O}_3$ : 1 to 60 mole%
    - 10 wherein M represents at least one metal selected from the group consisting of zinc, copper, silver, cobalt, nickel, iron, titanium, barium, tin and zirconium, and n represents a valence of metal; and
    - (b) at least one component selected from the group consisting of (i) oxidizing agents, (ii) plant extracts, and (iii) germicides.
  - 15 2. A deodorizer composition as claimed in claim 1, wherein the weight ratio of the components (a)/(b) is from 1/99 to 99.99/0.01.
  3. A deodorizer composition as claimed in claim 1 or 2, wherein said oxidizing agent is an organic peracid or a salt thereof, a percarbonate, or a persulfate.
  4. A deodorizer composition according to claim 1 or 2, wherein the plant extract is selected from among
    - 20 red algae, brown algae, gymnosperms and angiosperms.
    5. A deodorizer composition as claimed in claim 1 or 2, wherein the germicide is a sublimable substance.
    6. A deodorizer composition as claimed in claim 1 or 2, wherein the germicide is p-chloro-m-xlenol, butyl-m-cresol, o-phenylphenol or  $\alpha$ -bromocinnamic aldehyde.

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# EUROPEAN SEARCH REPORT

Application Number

EP 89 31 1296

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	GB-A- 895 683 (BORG-WARNER CORP.) * Page 1, lines 54-61,85-86; claims *	1,3	A 61 L 9/01
X	FR-A-1 428 096 (AMERICAN CYANAMID CO.) * Examples 1-3 *	1,3	
X	FR-A-2 485 034 (SOCIETE D'ETUDES ET DE REALISATIONS INDUSTRIELLES ET COMERCIALES SA) * Page 2, lines 12-21; claims 1-4 *	1,5	
X	EP-A-0 201 209 (OIL-DRI CORP. OF AMERICA) * Examples 1-3; claims 1-2,10,12 *	1,5	
D,A	EP-A-0 282 287 (LION CORP.) * Page 3, lines 6-50; examples 1-17 * & JP-A-63 220 874	1	
A	WO-A-8 101 643 (MOLECULAR SIEVE SYSTEMS) -----		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			A 61 L
Place of search THE HAGUE		Date of completion of the search 06-04-1990	Examiner ESPINOSA Y CARRETERO M.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	